

PATENT SPECIFICATION

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(54) COUPLING AGENT COMPOSITION

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to coupling agent compositions and to products obtained by using them.

Coupling agents have traditionally been applied to reinforcing materials which are to be laminated to or composited with a plastics material. These coupling agents enhance the strength of the laminates or composites. It is generally recognized that the performance of a coupling agent has a direct bearing on the strength of a laminate or composite. Therefore, the development of new, more effective coupling agent is of paramount importance to the plastics industry.

This invention relates to coupling agent formulations comprising metal oxide coated colloidal silica sols and organofunctional silanes as their two essential components; and to reinforcing fillers coated with such formulations.

Certain organo functional silane complexes

are well known in the plastics forming arts as excellent coupling agents for bonding organic resins to reinforcing filler materials.

The reinforcing filler materials used in the laminating and compositing arts can be treated with coupling agent formulations during, or subsequent to, their manufacture.

Coupling agent formulations have traditionally been applied to reinforcing filler materials as either a "finish" or a "size". A finish solution usually contains only a coupling agent formulation and an appropriate solvent. Such finishing solutions are usually applied to woven goods which are the preferred type of reinforcing material where maximum strength laminates are desired or required.

A more economic and convenient method for applying the coupling agent to reinforcing filler materials is the treatment of such materials with a size containing the coupling agents as an integral step in their manufacture. The sizing solution, containing both coupling agents and other processing additives, is applied to the reinforcing filler materials by spraying or padding techniques. Because the size is intended to perform a plurality of functions (for example, to bond multifilamentous glass fibrils into coherent strands, to protect such materials from self-abrasion and chemical degradation during handling and weaving, and to couple the reinforcing materials to the organic resins), it

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can contain, and often does, several components in addition to the coupling agents. The classical sizing solution for glass fibres routinely contains organic resinous bonding agents, lubricants, anti-static agents, emulsifiers, and coupling agents.

- 5 Unfortunately, the effectiveness of the coupling agent is generally somewhat offset by the presence of the other size components. Apparently the various components of the size randomly coat reinforcing filler material, leaving some sections of the materials devoid of coupling agents and therefore causing incomplete bonding of the reinforcing filler to the resin.

- 15 We have discovered that the addition of a positively charged sol to a solution containing a conventional organofunctional silane coupling agent in which the solvent is miscible with the disperse phase of the sol substantially enhances the wetting of the reinforcing filler materials with the resins and also substantially reduces the amount of silane needed in such a formulation to achieve comparable or superior results. Use of the coupling agent formulation of the invention improves the strength of the reinforcing filler-resin laminates or composites, and provides laminates and composites of greater translucence than conventional coupling agents.

- 30 Accordingly the present invention provides a coupling agent composition which comprises:

- (A) (i) a silane of the formula:



- 35 wherein each of the groups R, which may be the same or different, represents an alkyl radical having 1 to 18 carbon atoms, an alkenyl radical having 2 to 18 carbon atoms, a carboxyalkenyl radical having 3 to 18 carbon atoms, an alkenylcarboxyalkyl radical having 4 to 18 carbon atoms, an aminoalkyl radical having 1 to 18 carbon atoms, a mercaptoalkyl radical having 1 to 18 carbon atoms, an epoxy-substituted alkyl radical having 3 to 20 carbon atoms or an epoxy-substituted alkoxyalkyl radical having 4 to 20 carbon atoms; each of the groups X, which may be the same or different, represents a halogen atom or a hydroxy, alkoxy of 1 to 6 carbon atoms, aryloxy of 6 to 10 carbon atoms or amino radical; and n is an integer from 1 to 3, and (ii) a positively charged sol having a solids content of 5 to 50% by weight and comprising colloidal particles 2 to 100 millimicrons in size obtained by coating a silica core with a polyvalent-metal oxide, hydroxide or hydrated oxide; and (B) a reaction product of (i) and (ii). Preferably the weight ratio of silane (i) to sol solids is from 1:6 to 30:1, especially 1:3 to 10:1. A preferred embodiment of this agent is one in which each of the groups R which may be the same or differ-

ent represents an alkyl radical having 1 to 18 carbon atoms an alkenyl radical having 2 to 18 carbon atoms, an alkenylcarboxyalkyl radical having 4 to 18 carbon atoms, an aminoalkyl radical having 1 to 18 carbon atoms, a mercaptoalkyl radical having 1 to 18 carbon atoms or an epoxy-substituted alkyl radical having 3 to 20 carbon atoms.

A particularly preferred embodiment of this invention is a coupling agent which comprises (A) (i) a silane of the formula



wherein each of the groups R, which may be the same or different, represents an alkyl radical having 1 to 18 carbon atoms, a carboxyalkenyl radical having 3 to 18 carbon atoms, an alkenylcarboxyalkyl radical having 4 to 18 carbon atoms, an aminoalkyl radical having 1 to 18 carbon atoms, a mercaptoalkyl radical having 1 to 18 carbon atoms, or an epoxy-substituted alkyl radical having 3 to 20 carbon atoms; each of the groups X, which may be the same or different, represents a halogen atom, or a hydroxy, alkoxy of 1 to 6 carbon atoms, aryloxy of 6 to 10 carbon atoms, or amino radical and n is an integer from 1 to 3, and (ii) a positively charged alumina coated colloidal silica aquasol having a particle size of from 2 to 100 millimicrons and a solids content of 10 to 50% by weight and (B) a reaction product of (i) and (ii). In this embodiment the weight ratio of silane (i) to sol solids is 1:4 to 50:1, especially 1:3 to 3:1. The silane used in this embodiment is preferably γ -methacryloxypropyltrimethoxysilane, γ -aminopropyltriethoxysilane or vinyltriethoxysilane.

As used in this Specification the term "alkyl" is to be understood in its broad sense as including "cycloalkyl", where the number of carbon atoms permits.

The positively charged sols used comprise colloidal silica particles ranging in size from 2 to 100 millimicrons. The particles have a silica core coated with a polyvalent-metal oxide, hydroxide or hydrated oxide herein after referred to as a polyvalent-metal-oxygen compound. Typical polyvalent metals which may be employed in these sols are aluminium, chromium, titanium, or zirconium. These sols are stable on the acid side and have a high positive charge as opposed to the more traditional silica sols which are negatively charged and stable primarily on the basic side. These sols contain from 5 to 50% by weight of solid. Positively charged coated colloidal silica sols having water as the disperse phase are described in detail in U.S. Patent Specification No. 3,007,878. Sols having a disperse phase other than water, such as hydroxy-substituted alkanes of 1 to 6 carbon atoms, may also be used.

The compositions of this invention can be

incorporated into size and finish solutions which may or may not include other processing additives, notably, organic resinous bonding agents, lubricants, anti-static agents, and emulsifiers.

The sizing and finishing compositions of the invention are useful in preparing reinforcement filler materials for bonding to organic resins.

The relative weight ratio of organofunctional silane to positively charged aquasol solids in the coupling agent formulations of this invention are not critical but as a practical matter will generally range from 1:6 to 30:1, preferably, from 1:3 to 10:1. However, the weight ratios of the respective components of the composition will change upon their being admixed because positively charged silica sol and organofunctional silane partly react to form a third, as yet unidentified, compound.

Diminution in the concentration of organofunctional silane by limited addition of, or part replacement, by less expensive polyvalent-metal oxide coated silica sols will not result in a sacrifice of bonding strength. Substitution of 10 to 70% by weight of the organofunctional silanes of conventional coupling agents by a polyvalent-metal oxide coated silica sol will yield comparable, and in some instances improved bonding strengths. The observation of comparable or superior bonding capacity is believed to be attributable to a synergism between the two components; the positively charged colloidal silica sols having a greater affinity for the reinforcement materials (most reinforcement materials being negatively charged), than silane alone and therefore causing more complete wetting of such materials with resins. The synergism is especially evident where the reinforcing materials are "low sodium" glasses.

Formulations having a ratio of a 30% solids positive aquasol to silane of about 3 are preferred for the formulations of this invention both from the standpoint of economics and performance.

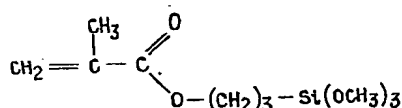
Coupling Agent Formulation Components

The positively charged sols of this invention preferably are aquasols of positively charged colloidal particles consisting of a dense silica core coated with a polyvalent metal-oxygen compound which is a metal oxide, hydroxide, or hydrated oxide. The pH of the sols useful in this invention generally ranges from 2.5 to 7. Outside this range the sols tend to be unstable. The negatively charged colloidal silica is coated with a sufficient amount of the metal-oxygen compound to impart a positive charge on the resulting colloidal polyvalent metal-oxygen compound coated silica. The metals useful for preparing these sols have a valence of 3 to 4. Examples are aluminum, chromium, titanium, and zir-

conium. These sols are described in, for example, U.S. Patent Specification No. 3,007,878. These aquasols are acidic, have a particle diameter from 2 to 100 millimicrons and have from 5 to 50% solids. Alumina coated silica aquasols are preferred in the compositions of this invention. Other useful solvents are hydroxy-substituted alkanes of 1 to 6 carbon atoms.

Organofunctional silane selection is based on the readiness of the organofunctional silane to promote adhesion between filler and the specific resin. For example, gamma-methacryloxypropyltrimethoxy-silane is one of the preferred coupling agents for glass-polyester composites or laminates. A gamma-aminopropyltriethoxysilane agent coupling gives strong epoxy resin glass composites or laminates but gives inferior polyester glass composites or laminates. The general approach for selection of organofunctional silane is to match the organic portion of the molecule to the resin being used in the composite or laminate.

The preferred organofunctional silanes in these coupling agent formulations are gamma-methacryloxypropyltrimethoxysilane,



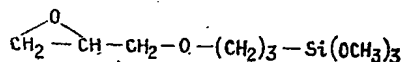
vinyltriethoxysilane,

gamma-aminopropyltriethoxysilane,
 $\text{H}_2\text{N}-(\text{CH}_2)_3-\text{Si}(\text{OC}_2\text{H}_5)_3$,

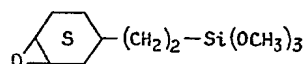
vinyl-tris(2-methoxyethoxy) silane,

$\text{CH}_2 = \text{CH}-\text{Si}(\text{OC}_2\text{H}_4\text{OCH}_3)_3$,

gamma-glycidyloxypropyltrimethoxysilane,



and beta - (3,4 - epoxycyclohexyl)ethyltrimethoxysilane



Additives which have been traditionally added to sizes or finishes can also be used in conjunction with the coupling agent formulations of this invention to make size and finish compositions. The primary purpose of these additives is not related to coupling the reinforcing materials to the resins but rather to the processing and handling of the re-

inforced materials themselves.

The silane and the positively charged sol can be mixed directly with each other or they can be combined by adding them to an aqueous or a polar organic solvent which dissolves the silane and is miscible with the disperse phase of the sol. The selection of an appropriate solvent will depend upon the relative solubility of all the various components in the formulation and the type of materials being sized or finished. It will be appreciated that the disperse phase of the sol and the solvent may be the same, e.g. water. The organofunctional silane concentration of the coupling agent composition can range from 0.05 to 10.0 parts by weight of silane to each 100 parts by weight solvent. As noted earlier the organofunctional silanes and metal oxide coated silica sols partly react when admixed to form a third, as yet unidentified, compound. After an initial reaction between components (i) and (ii) to form the third component (B), the solution remains quite stable and has a relatively long pot life.

The coupling agent compositions of this invention can be incorporated into a size in place of the silane alone and applied to the reinforcing filler materials by any of the conventional sizing techniques.

The coupling agent can also be applied in a finish to woven materials where it may be the only functional component present.

After coating of the reinforcing filler materials with a sizing or finishing solution the coated materials are dried, generally heat cured, for a period of from a few minutes to several hours depending on the temperature. The preferred drying temperatures range from 50 to 180°C. In general the time required to complete polymerization of the composition will vary inversely with the temperature.

A typical reinforcing material is a substance which when incorporated into and coupled to the organic resins by the process of this invention enhances the strength and stiffness of the cured plastics material. The reinforcement materials of this invention can be in the form of rovings, fabrics, continuous and chopped-strand mat, chopped strands and milled fibres. Among the reinforcing materials used in the laminate or composite forming arts are fibres of pure fused silica, refractory aluminosilicate, glass fibres, rock wool fibres, asbestos, sisal, cotton, quartz, glass microspheres, graphite and boron fibres and metal whiskers.

As is evident from the list of common reinforcing materials many of the substances are quite distinct in their physical characteristics, (density, surface area and porosity). The physical characteristics of the reinforcement materials will determine the amount of coupling agent formulation adsorbed or absorbed and therefore the relative strength of the bond between the coupling agent and

the reinforcement materials. The amount of coupling agent actually present on the reinforcing materials can be controlled by regulating the wet weight pick-up, the concentration of the essential components in the formulation, and by controlling the amount of surface area of the reinforcing material. The concentration of components (i) and (ii) and (B) of the coupling agent formulation on the reinforcing materials will range from 0.01 to 20.0% by weight of such materials. Preferably the amount of coupling agent will not exceed 0.25 to 10.0% of the weight of the reinforcing materials. Low surface area and low porosity materials, such as glass fibres, pick up relatively low amounts of these coupling agent formulations.

Non-reinforcing filler materials can also be incorporated into the resinous composites or laminates formed with the coupling agent formulations of this invention, either for reasons of economics (substitution of cheaper materials for expensive resins) or to impart colour or other properties to the plastics material.

Among the more common of the non-reinforcing filler materials which can be used are kaolin, talc, mica, chrysotile asbestos, alumina, zircon, zirconia, magnesium oxide, colloidal amorphous silica, attapulgite, wollastonite, pearlite, flyash, calcium silicate, synthetic fillers and fibres, and in general any particulate refractory material.

The amounts of reinforcing filler materials which can be incorporated into a resinous composite can vary from as little as 1 to as much as 90% by weight of the total composition, depending on the relative density of the resin and the reinforcing materials and on the method of fabrication. For example, filament glass fibre structures can be prepared having extremely high loadings of glass relative to resin. The concentration of reinforcing fillers in the majority of the composites will range from 10 to 70% by weight of the total resin composite.

The organic resins, as distinguished from the resinous bonding agents of the sizing formulations, are liquid, semi-solid or solid materials produced by union (polymerization or condensation) of a large number of molecules of one, two, or less frequently three, relatively simple compounds. The term "resin" as used herein embraces both the synthetic and chemically modified natural resins. These resins generally have low physical strengths, which are improved by forming composites with inert fillers.

Thermoplastic resins which can be used to prepare composites with inert fillers and the coupling agent compositions of this invention include polycarbonamide resins, thermoplastic polyester resins, poly[glycol(dimethylterephthalate)], polyacrylonitrile, linear and low density poly-

ethylene, polypropylene, polybutadiene, polycarbonates, polyphenylene oxide, polysulphones, polyvinyl chloride, polystyrene and polyurethane.

5 Composites containing thermoplastics may be prepared by heating the thermoplastic and causing the thermoplastic to flow, thus wetting the filler or reinforcing material. The hot composite is cooled and the composite becomes stiff. If a thermoplastic composite is heated to the softening points of the polymer, the composite will be soft.

10 Thermosetting resins which can be used to make laminates using the coupling agents of this invention include polyester resins which are cross-linkable through vinyl unsaturation, such as maleic acid-glycol copolymers and combinations of these with styrene, epoxy, phenolformaldehyde, urea formaldehyde, melamine formaldehyde, polyimide, acrylic and methacrylic resins. The uncured thermosetting plastic syrup and the filler or reinforcing material are combined and the mixture is heat cured. The resulting laminate becomes hard at the curing temperature.

25 Treated reinforcement materials of this invention may be used to reinforce various elastomers such as natural rubber, oil extended rubber and a variety of butadiene, styrene, acrylonitrile, and polyacrylate modifications of synthetic and natural rubber.

30 The selection of the plastics material for a composite depends upon the end use of the composite. That is no one plastics material is used for all applications. Glass filled polyethylene offers inexpensive composites. Epoxy laminates are highly chemical resistant. Polyimide laminates can be used for high temperature application.

40 The following Examples illustrate the present invention. Parts and percentages are by weight unless otherwise specified. The sols used in the Examples, are, unless otherwise stated, positively charged sols having a solids content of 5 to 50%, by weight and comprising colloidal particles 2 to 100 millimicrons in size obtained by coating a silica core with a polyvalent metal oxide, hydroxide or hydrated oxide. The silanes used in the Examples have the formula R_nSiX_{4-n} as hereinbefore defined.

Example 1.

55 Methacrylyloxpropyltriethoxysilane and a 30 weight percent aqueous alumina-modified silica sol were added to 100 parts of water

and this solution was stirred for one hour at a pH of 4.7. The alumina-modified silica sol, prepared by mixing an aqueous solution of basic aluminium chloride with an aqueous silica sol, heating the mixture at 70°C. for 1 hour, and then adding magnesium oxide to raise the pH of the resulting sol to 4.4, contained 26% SiO_2 , 4% Al_2O_3 , 1.4% Cl, and 0.2% MgO , and had an approximate particle diameter of 16 millimicrons. The total of the silane and alumina-modified silica sol was 2 parts. The ratio of alumina-modified silica sol used per mole of silane is given in Table I. The water also contained 4 parts of a 55% aqueous emulsion of a polyvinyl acetate (Elvacet 81-900, manufactured by E. I. du Pont de Nemours and Company of Wilmington, Delaware) and 0.1 part of a lubricant (Citrasol (Registered Trade Mark) 220, purchased from ICI America Inc., Stamford, Conn.). The coupling agent formulation was prepared by adding the respective components to the solvent sequentially, the particular order being unimportant.

Heat cleaned glass cloth was dipped into the coupling agent solution and after wringing out was dried in an oven. After cutting to proper length and width, the treated glass was ready for laminate fabrication.

A 1/8 inch thick 12-ply laminate was prepared by placing a piece of the treated fabric on a puddle of polyester resin derived from 1 mole of phthalic anhydride, 1 mole of maleic anhydride and 2.2 moles of propylene glycol esterified to an acid number of between 30 and 45. A polyester resin of this description is available under the trade name of "Paraplex" (Registered Trade Mark) P-43 manufactured by Rohm and Haas of Philadelphia. One hundred parts of the polyester resin was catalyzed with 1 part of benzoyl peroxide. After the fabric had become wet by wicking the resin, an additional quantity of resin was poured on top of the fabric layer and another piece of fabric was added. This procedure is repeated until the laminate had 12 thicknesses of glass fabric. The laminate was covered with cellophane [Registered Trade Mark] and the excess resin and air was removed by squeegeeing the laminate.

After heat curing under pressure the laminate was cut into test specimens. The test specimens are tested for flexural dry strength and short-term flexural wet strength after 2 hours in boiling water. The results are tabulated below in Table I.

TABLE I

Ratio Alumina Coated Silica Sol (parts)	Flexural Strength (10 ³ psi)	
	Dry	2 hr Boil
Silane (parts)		
0	79.3	71.4
0.008	81.9	73.7
0.015	83.8	75.2
0.06	84.9	76.1
0.15	84.0	75.5
0.3	77.7	67.2
0.6	75.6	59.0
∞	75.0	41.2

Example 2.

Heat cleaned glass rovings are treated with a coupling agent solution containing X parts of (partly) hydrolyzed methacrylyloxypropyltriethoxysilane (the methacrylyloxypropyl group remains in the hydrolysed silane) and Y parts of the alumina coated silica sol of Example 1. The solution also contains 2% of a 55% aqueous emulsion of polyvinyl acetate and 0.1% of a lubricant. The rovings are wrung out and dried in an oven. The treated rovings are cut into 30 inch pieces and 6 grams

of the roving sections are tied in the middle with a copper wire. These glass rovings are soaked in a polyester resin solution containing 1.5 parts of benzoyl peroxide, 15 parts of styrene and 135 parts of polyester resin. The soaked glass rovings are drawn into a 4mm. glass tube and oven cured. The rod laminates are removed from the glass tubes and cut into test specimens and tested for flexural dry strength and short term flexural wet strength after 2 hours in boiling water. The results are tabulated below in Table II.

TABLE II

X Parts Silane	Y Parts Alumina Coated Silica Sol of Example 1	Flexural Strength (10 ³ psi)	
		Dry	2 hr Boil
0.25	0	179	145
0.25	0.25	194	161
0.10	0.40	187	158
0.50	0	178	159

The results of this testing show that the silane concentration can be reduced to a fifth by replacing silane by an equal amount of alumina coated silica sol and still maintain a given level of strength after 2 hours boiling.

Example 3.

Three different alumina coated positive sols containing silica particles having surface mole

ratios of silica to alumina of 1:2, 1:1, and 2:1 were prepared and used in turn in the coupling agent solution as described in Example 2 (replacing the sol used therein). The solution was applied to glass rovings as described in Example 2. These glass rovings were used to prepare polyester rod composites. All three of these different positive sols gave polyester glass rod composites of comparable strength.

Surface silica:Aluminium	Flexural Strength (10 ³ psi)	
	Dry	2 Hour Boil
1 : 2	178	166
1 : 1	182	154
2 : 1	188	160

Example 4.

The starting materials (basic aluminium chloride and colloidal silica sols) for the preparation of the positive sols described in Example 3 were added to the coupling agent bath described in Example 2 again replacing the sols used therein. The polyester glass composites prepared from rovings treated with a coupling agent solution containing the starting materials, a hydrolyzed organofunctional silane as used in Example 2, polyvinyl acetate, and lubricant were not as strong as the laminates prepared with alumina coated silica sol, the organofunctional silane, polyvinyl acetate, and lubricant.

Example 5.

Heat cleaned glass cloth was treated with a coupling agent solution containing gamma-aminopropyltriethoxysilane, polyvinyl acetate,

lubricant and positive alumina coated silica sol. This treated glass cloth is used to prepare an epoxy laminate. The epoxy resin is a reaction product of epichlorohydrin and bisphenol-A and a curing agent of meta-phenylenediamine is used. After exposure to boiling water for 72 hours, the laminates prepared from the coupling agent solution containing the alumina coated silica sol are much stronger than laminates prepared from an otherwise similar coupling agent solution but containing no alumina coated silica sol.

Example 6.

Using the method of Example 2 the amount of silane to give a desired level of reinforcement can be cut by 50% when positive sol is added to the coupling agent solution and when vinyltriethoxysilane is substituted for gamma-methacrylyloxypropyltriethoxysilane.

Positive Sol (%)*	Vinyl Silane (%)	Flexural Strength (10 ³ psi)	
		Dry	2 Hour Boil
0.1	0.1	182	147
—	0.2	183	151

* Size bath concentration

Example 7.

Glass filled polyethylene is made stronger by adding to the coupling agent solution a small amount of positive sol. Aside from the solvent and the alumina coated silica sol, the major constituent in the coupling agent solution is the silane. Besides enhanced strength after exposure to boiling water, the coupling agent solution with the alumina coated silica sol impart further properties to the glass which are advantageous in the formation of glass filled polyethylene. The glass with the alumina coated silica sol coating allows easier formation of the glass filled polyethylene, that is, there is faster wet-out of the glass fibres and a lower working temperature. A similar effect is observed when reinforcing polyvinyl chloride with alumina coated silica sol treated glass.

Example 8.

Asbestos treated with the coupling agent solution described in Example 1 and with an aluminium (as Al₂O₃) to silane ratio of 0.2 gave a treated asbestos product which is easily dispersed in polyester resin. When the alumina coated silica sol is not present in the coupling agent solution the asbestos does not disperse as easily in the polyester resin. Laminates prepared from polyester resin and the treated asbestos were strong. The asbestos treated with alumina coated silica sol containing solution gives the stronger laminate.

Examples 9—15.

The following Examples demonstrate the wide utility of a silane-alumina coated silica sol coupling agent of the invention over the

- 5 use of a silane by itself. In all of these Examples the coupling agent solution containing both silane and alumina coated silica sol gives stronger composites or laminates than the coupling agent solutions containing only silane. In addition to the stronger laminates
- 10 obtained from the invention, the materials coated with the coupling compositions containing alumina coated silica sol are easier to process and give composites and laminates of higher clarity. The reinforcing agent and resins used are given in the Table below.

TABLE 3

Example	Reinforcing Agent	Resin
9	glass microspheres	polypropylene
10	mica	polyester
11	mica	polyimide
12	graphite fibres	epoxy
13	glass rovings	polystyrene
14	glass cloth	polycarbonate
15	cotton	urea formaldehyde

WHAT WE CLAIM IS:—

- 15 1. A coupling agent composition which comprises

(A) (i) a silane of the formula:



- 20 wherein each of the groups R, which may be the same or different, represents an alkyl radical having 1 to 18 carbon atoms, an alkenyl radical having 2 to 18 carbon atoms, a carb-
oxyalkenyl radical having 3 to 18 carbon atoms, an alkenylcarboxyalkyl radical having
25 4 to 18 carbon atoms, an aminoalkyl radical having 1 to 18 carbon atoms, a mercaptoalkyl radical having 1 to 18 carbon atoms, an epoxy-substituted alkyl radical having 3 to 20 carbon atoms or an epoxy-substituted alkoxyalkyl radical having 4 to 20 carbon atoms; each of
30 the groups X which may be the same or different, represents a halogen atom or a hydroxy, alkoxy of 1 to 6 carbon atoms, aryloxy of 6 to 10 carbon atoms or amino radical; and n is an integer from 1 to 3, and (ii) a
35 positively charged sol having a solids content of 5 to 50% by weight and comprising colloidal particles 2 to 100 millimicrons in size obtained by coating a silica core with a poly-
40 valent-metal oxide, hydroxide or hydrated oxide; and (B) a reaction product of (i) and (ii).

2. A composition according to claim 1 wherein the disperse phase of the sol (ii) is water or a hydroxy-substituted alkane of 1 to 6 carbon atoms.

3. A composition according to claim 1 or 2 wherein the sol has a pH of 2.5 to 7.

4. A composition according to any one of

the preceding claims wherein the polyvalent metal is aluminium, chromium, titanium or zirconium.

5. A composition according to claim 4 wherein the positively charged sol (ii) is an alumina coated colloidal silica aquasol.

6. A composition according to any one of the preceding claims wherein the silane (i) is gamma - glycidyloxypropyltrimethoxysilane, gamma - methacrylyloxypropyltrimethoxysilane, vinyltriethoxysilane, gamma-amino-propyltriethoxysilane, beta - (3,4 - epoxycyclohexyl)ethyltrimethoxysilane or vinyltris (2-methoxyethoxy)silane.

7. A composition according to any one of the preceding claims which contains a solvent for the silane which is miscible with the disperse phase of the sol, there being 0.05 to 10.0 parts by weight of silane per 100 parts by weight of the solvent.

8. A composition according to any one of the preceding claims wherein the weight ratio of silane (i) to sol solids is from 1:6 to 30:1.

9. A composition according to claim 8 wherein the weight ratio is 1:2 to 10:1.

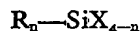
10. A composition according to any one of claims 1 to 7 wherein each of the groups R which may be the same or different represents an alkyl radical having 1 to 18 carbon atoms, an alkenyl radical having 2 to 18 carbon atoms, an alkenylcarboxyalkyl radical having 4 to 18 carbon atoms, an aminoalkyl radical having 1 to 18 carbon atoms, a mercaptoalkyl radical having 1 to 18 carbon atoms or an epoxy-substituted alkyl radical having 3 to 20 carbon atoms.

11. A composition according to claim 10

wherein the positively charged sol is an aquasol and wherein the weight ratio of silane (i) to sol solids is from 1:6 to 30:1.

12. A composition according to claim 11 wherein the weight ratio is 1:3 to 10:1.

13. A coupling agent composition which comprises (i) a silane of the formula



wherein each of the groups R, which may be the same or different, represents an alkyl radical having 1 to 18 carbon atoms, a carboxy-alkenyl radical having 3 to 18 carbon atoms, an alkenylcarboxyalkyl radical having 4 to 18 carbon atoms, an aminoalkyl radical having 1 to 18 carbon atoms, a mercaptoalkyl radical having 1 to 18 carbon atoms or an epoxy-substituted alkyl radical having 3 to 20 carbon atoms; each of the groups X, which may be the same or different represents a halogen atom, or a hydroxyl, alkoxy of 1 to 6 carbon atoms, aryloxy of 6 to 10 carbon atoms or amino radical and n is an integer from 1 to 3, and (ii) a positively charged alumina coated colloidal silica aquasol having a particle size of from 2 to 100 millimicrons and a solids content of 10 to 50% by weight and (b) a reaction product of (i) and (ii).

14. A composition according to claim 13 wherein the weight ratio of silane (i) to sol solids is 1:4 to 50:1.

15. A composition according to claim 14 wherein the weight ratio is 1:3 to 3:1.

16. A composition according to any one of claims 13 to 15 wherein the silane is γ -methacryloyloxypropyltrimethoxysilane, γ -aminopropyltriethoxysilane or vinyltriethoxysilane.

17. A composition according to claim 1 substantially as described herein.

18. A composition according to claim 1 substantially as described in Example 2 or 6.

19. A composition according to claim 1 substantially as described in any one of Examples 1, 3 to 5 and 7.

20. A process for coating reinforcement material for an organic resin which comprises (a) coating the reinforcement material with a coupling agent composition as claimed in any one of claims 1 to 9 and 17, the amount of the composition being such that there is 0.01 to 20.0% by weight of (A) and (B) based on the weight of the reinforcement material and (b) heating the coated material.

21. A process according to claim 20 wherein the reinforcement material is fibreglass.

22. A process for coating reinforcement material for an organic resin which comprises (a) coating the reinforcement material with a coupling agent composition as claimed in any one of claims 10 to 12 and 18, the amount of the composition being such that there is 0.01 to 20.0% by weight of (A) and (B) based

on the weight of the reinforcement material and (b) heating the coated material.

23. A process according to claim 22 wherein the reinforcement material is fibreglass.

24. A process for coating reinforcement material for an organic resin which comprises (a) coating the reinforcement material with a coupling agent composition as claimed in any one of claims 13 to 16 and 19, the amount of the composition being such that there is 0.01 to 20.0% by weight of (A) and (B) based on the weight of the reinforcement material and (b) heating the coated material.

25. A process according to claim 24 wherein the reinforcement material is fibreglass.

26. A process according to claim 20, 22 or 24 substantially as hereinbefore described.

27. A process according to claim 24 substantially as described in any one of Examples 1, 3 to 5 and 7.

28. A process according to claim 22 substantially as described in Example 2 or 6.

29. Reinforcement material for an organic resin whenever coated by a process claimed in claim 20, 21 or 26.

30. Reinforcement material for an organic resin whenever coated by a process claimed in claim 22, 23 or 28.

31. Reinforcement material for an organic resin whenever coated by a process claimed in claim 24, 25 or 27.

32. A process for coupling an organic resin to reinforcement material therefor which comprises contacting reinforcement material as claimed in any one of claims 29 to 31 with the organic resin.

33. A process according to claim 32 wherein the organic resin is any one of those specifically identified herein as such.

34. A process for coupling an organic resin to reinforcement material therefor which comprises contacting reinforcement material as claimed in claim 30 with the organic resin.

35. A process for coupling an organic resin to reinforcement material therefor which comprises contacting reinforcement material as claimed in claim 31 with the organic resin.

36. A process according to claim 32 substantially as hereinbefore described.

37. A process according to claim 32 substantially as described in any one of Examples 1, 3 to 5 and 7 to 15.

38. A process according to claim 32 substantially as described in Example 2 or 6.

39. Organic resin coupled to reinforcement material therefor by a process claimed in any one of claims 32, 33 or 36.

40. Organic resin coupled to reinforcement material therefor by a process claimed in claim 34 or 38.

41. Organic resin coupled to reinforcement material therefore by a process claimed in claim 35 or 37.

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